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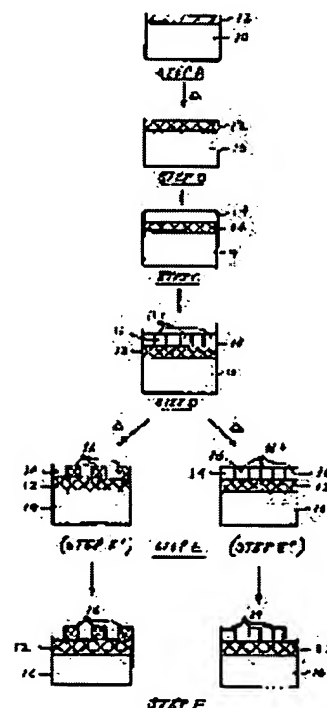
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## (54) HALATION PREVENTIVE COMPOSITION

### (57)Abstract:

**PURPOSE:** To absorb incident exposure light radiation and reflected exposure radiation and to enable the attenuation of standing waves by incorporating a binder resin and a crosslinking agent compd. which can induce a thermally activated crosslinking reaction with the binder resin into a halation preventive compsn.

**CONSTITUTION:** The halation preventive compsn. is applied on a substrate 10 in order to impart a halation preventive coating layer 12 in a step A. The halation preventive layer is partially cured in a step B. A photoresist is applied on the halation preventive layer 12 in a step C. Images are formed on a coating layer 14 by activating radiation to generate the pattern forming images 16 in the layer 14 in a step D. The photoresist is subjected to heating after exposure in a step E. The exposed resist coating layer 14 is



developed by using an aq. basic developer, such as inorg. alkali in a step F. The final heating and drying of the acid solidified photoresist is executed in order to further cure the developed exposure areas 16.

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## CLAIMS

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### [Claim(s)]

- [Claim 1] Said constituent which is an antihalation constituent which can form a finishing photoresist layer and an enveloping layer made to construct a bridge, and contains a cross linking agent compound with said constituent able to trigger thermal activation crosslinking reaction of a resin binder and said resin binder.
- [Claim 2] A constituent according to claim 1 said whose resin binder is a binder which used a phenol as a principal component.
- [Claim 3] A constituent according to claim 1 said whose cross linking agent compound is the material which used an amine as a principal component.
- [Claim 4] A constituent according to claim 1 which contains further a compound chosen from a group who consists of an acid and an acid generator compound.
- [Claim 5] A constituent containing a silicon content material according to claim 1.
- [Claim 6] A constituent according to claim 1 which contains a radiation absorbent color further.
- [Claim 7] A constituent according to claim 1 said whose antihalation constituent is non-light image formation nature intrinsically.
- [Claim 8] Said substrate with which it is a substrate which has an antihalation constituent enveloping layer on it, and the coat substrate which has a photoresist enveloping layer on said antihalation constituent enveloping layer, and said photoresist contains a resin binder and a radiation susceptibility component including a cross linking agent compound with said antihalation constituent enveloping layer able to trigger thermal activation crosslinking reaction of a resin binder and said resin binder.
- [Claim 9] A substrate according to claim 8 selectively stiffened at least by said antihalation constituent enveloping layer with heat.
- [Claim 10] A substrate according to claim 8 over which a part of the antihalation constituent organic enveloping layer [ at least ] is made to construct a bridge with said a part of photoresist enveloping layer [ at least ].
- [Claim 11] A method for processing a substrate characterized by providing the following (a) A phase which applies a layer of an antihalation constituent containing a cross linking agent compound which can trigger thermal activation crosslinking reaction of resin van IDA and said resin binder on said substrate (b) A phase of stiffening said antihalation constituent layer selectively at least (c) A phase which applies a layer of a resin binder and a photoresist constituent containing a radiation susceptibility component on said antihalation constituent layer (d) A phase which exposes said photoresist constituent layer (e) A phase of developing said exposed photoresist constituent layer
- [Claim 12] A method according to claim 11 of including further a phase which carries out stoving of the exposed resist coat substrate in front of said development phase.
- [Claim 13] A method according to claim 11 of making sufficient temperature triggering crosslinking reaction between said resin binder of said antihalation constituent, and said cross linking agent compound harden said antihalation constituent layer selectively at least by heating said antihalation constituent layer.

[Claim 14] A way according to claim 12 said stoving makes said a part of antihalation constituent layer construct a bridge to said a part of photoresist layer.

[Claim 15] A way according to claim 11 said antihalation constituent contains further a compound chosen from a group who consists of an acid and an acid generator compound.

[Claim 16] A way according to claim 11 said antihalation constituent contains a heat acid generator further.

[Claim 17] A method according to claim 11 of being the material which is chosen from a group to whom said cross linking agent compound of said antihalation constituent changes from resin which used benzoguanamine as a principal component, and resin which used a melamine as a principal component and which used an amine as a principal component.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the constituent which reduces an echo of the exposure radiation from the substrate which is behind the finished resist layer. Furthermore, especially this invention relates to the antihalation constituent characterized in one side by including the cross linking agent activated by heat.

[0002]

[Description of the Prior Art] A photoresist is used in order to imprint an image to a substrate. The enveloping layer of a photoresist is formed on a substrate and the resist layer is selectively exposed by the radiation source of activation radiation through a photograph mast after that. A photo mask has other transparent areas to an opaque area and activation radiation to activation radiation. The exposure to activation radiation brings about the chemical change of the photoresist coat induced by light, and imprints the pattern of a photo mask on a resist coat substrate by it. A photoresist is developed in order to give after exposure the relief image which enables alternative processing of a substrate.

[0003] A photoresist may be whichever of a positive type and a negative mold. such an enveloping layer portion exposed by activation radiation by most photoresists of a negative mold -- the form of the reaction between the photoactivation compound of the resist constituent, and a polymerization possible reagent -- a polymerization -- or a bridge is constructed. Therefore, the solubility in the inside of the developer solution of the exposed coat portion becomes lower than the solubility in the inside of the developer solution of the non-exposing portion. In the case of a positive type photoresist, although the solubility in a developer solution becomes higher in an exposure portion, on the other hand, there is solubility in a developer solution relatively in a non-exposing area until now [ low ]. The conventional technology of a photoresist By Deforest The work "a photoresist material and processing (Photoresist Materials and Processes)" (McGraw Hill Book Company, New York, ch.2, 1975) It sets and reaches. By Moreay, the work "semiconductor lithography, The principle, actual condition, and material (Semiconductor Lithography, Principles, Practices and Materials) It sets." (Plenum Press, New York, ch.2, and ch.4) It is explained. .

[0004] A photoresist is used mainly in semiconductor manufacture, in manufacture of such a semiconductor, it is a micron preferably or the semiconductor slice ground by altitude like silicon or gallium arsenide is targeted for the thing which achieve circuitry and which is changed into the complicated matrix of the electronic conduction path of geometry smaller than a micron. It is an important means for proper photoresist processing to attain this object. although strong interdependence is between each photoresist processing phases, when obtaining the photoresist image of high resolution - exposure -- \*\* -- it is thought that it is one of the important phases.

[0005] An echo of the activation radiation used in order to expose a photoresist gives a big limit to the resolution of the image by which pattern formation is carried out in many cases into a resist layer. An echo of the radiation from a substrate / resist interface may generate fluctuation of the intensity of radiation in the resist under exposure, and may produce uneven photoresist line breadth as the result at

the time of development. Radiation may be scattered about from a substrate / resist interface, it may enter in the resist field where it does not have the intention of exposure, and fluctuation of line breadth may be similarly produced as the result. Typically, probably the amounts of dispersion and an echo differ for every field, and will produce fluctuation of the further line breadth as the result.

[0006] An echo of activation radiation contributes also to what is known as "a standing wave effect (standing wave effect)" in this work. In order to remove the effect of the chromatic aberration in an exposure device lens, radiation of monochrome or semi- monochrome is used with resist projection technology. However, when radiation of monochrome or semi- monochrome is used for photoresist exposure, an interference positive on account of the radiation echo in a substrate / resist interface and harmful is large. In such a case, the reflected light blocks incident light and produces a standing wave in the resist as the result. In the case of a substrate field reflecting to altitude, a problem is worsened although the standing wave of the large amplitude produces the resist thin layer of underexposure in the minimum wave therefore. The layer of such a underexposure may bar perfect resist development, and may cause the edge radicalization problem in a resist cross section. Generally the time amount needed for exposing a photoresist although the total quantity of the radiation needed for exposing the resist increases the more the more the amount of resists increases therefore is the increasing function of resist thickness. However, the exposure time also contains the harmonic component which changes continuously between maximum and the minimum value according to resist thickness on account of the standing wave effect. If resist thickness is non-homogeneity, the problem will become much more serious and will produce adjustment of adjustable line breadth as a result.

[0007] Fluctuation of a substrate configuration also produces the problem of the echo which restricts resolution. The radiation which collides with it causes scattering about or reflecting in the direction in which various control is impossible, and any images on a substrate have an adverse effect on the homogeneity of resist development. The effect of the reflected radiation becomes more serious as a substrate configuration becomes more complicated with the efforts which are going to design a more complicated circuit. For example, especially as for the metal wiring used on many micro electronic substrates, a problem is on account of the structural feature and a high reflection factor field by \*\*\*\*.

[0008] The problem of such a radiation echo has been coped with by being the wavelength used for exposing a photoresist, or adding the specific color which absorbs radiation near the wavelength to a photoresist constituent. The example of the color used such contains a coumarin group, a Methyl Orange, and the metanil yellow. That researcher has discovered how many things for which the resolution of the resist image with which pattern formation of the activity of such a color was carried out may be restricted.

[0009] Another solution was using the radiation absorption layer inserted between the substrate front face and the photoresist enveloping layer. For example, PCT by which explanation of all them about an acid-resisting (antihalation) constituent and its activity is included in this book as a reference matter Application Please refer to WO 90/03598, U.S. Pat. No. 4,910,122, 4,370,405, and 4,362,809. However, some conventional acid-resisting coats at least have a defect of the adhesive lack to the substrate front face located in a finishing photoresist layer and/or the bottom of it. Such an adhesive problem may reduce remarkably the resolution of the photoresist image by which pattern formation was carried out.

[0010] Therefore, probably, it will be desirable to obtain the antihalation coat constituent which absorbs incidence exposure radiation and reflective exposure radiation remarkably, and brings about remarkable attenuation of a standing wave. Furthermore, probably, it will be desirable to obtain the antihalation coat constituent which can be pasted up suitable for both the photoresist enveloping layer which can cover on a micro electronic substrate and is applied on the antihalation coat, and the substrate front face under the antihalation coat.

[0011]

[The technical problem and The means for solving a technical problem] which invention tends to solve This invention offers the antihalation constituent suitable for using it with a photoresist, and this antihalation constituent contains the compound which can generally trigger the crosslinking reaction of a resin binder and said resin binder induced by heat. Preferably, the component of this antihalation

constituent can construct a bridge with the finishing coat of a photoresist constituent, by it, increases adhesion between the two above-mentioned enveloping layers, and avoids the remarkable trouble of some conventional acid-resisting systems at least. Furthermore, the antihalation constituent of this invention contains the acid or acid generator compound which enables crosslinking reaction to carry out the catalyst of the reaction between said resin binders and said bridged compounds, and to go on at a relative more low temperature. The nomenclature "an acid generator (acid generator)" used in this book means the compound which generates an acid by the exposure or heat treatment for example, to activation radiation by suitable processing of the compound. The cross linking agent activated with heat is a material preferably like [ it is possible for them to be various materials and ] the resin which uses benzoguanamine as a principal component, and the resin which uses a melamine as a principal component which uses an amine as a principal component. Furthermore, in order to strengthen a radiation absorption property, one or more color compounds which absorb radiation of the exposure wavelength of a finishing photoresist or radiation near the wavelength can be included by the antihalation constituent of this invention.

[0012] Furthermore, this invention applies said antihalation constituent and offers the method for using said antihalation constituent with a photoresist. Therefore, in the desirable side, it is (a). Phase which applies the layer of the antihalation constituent of this invention on a substrate, (b) The phase stiffen this antihalation constituent enveloping layer selectively at least, and (c) The phase which applies a photoresist layer on this covered substrate, and (d) The phase which exposes the selection portion of that photoresist layer, and (e) The phase which carries out stoving of the applied antihalation enveloping layer and the photoresist enveloping layer, and (f) A method including the phase of developing the exposed photoresist layer is offered. When a suitable photoresist is used, the result of the stoving of the two above-mentioned enveloping layers is carried out to bridge formation between an antihalation constituent component and a photoresist constituent component. Pasting the substrate front face on which the antihalation constituent of this invention contains the substrate used for a micro electronic use good is also discovered.

[0013] Furthermore, this invention offers the formation method of a relief image and a new manufacture article which consists of the substrate covered with said antihalation constituent which was covered only with the antihalation constituent of this invention, or was combined with the photoresist constituent with it. The coat substrate with which the antihalation constituent of this invention is covered on the substrate, and a photoresist is covered on said antihalation constituent, and said photoresist contains resin van IDA and a radiation susceptibility component especially is offered.

[0014] The desirable antihalation constituent of this invention constructs a bridge by heat treatment, and contains the mixture of the material which can be hardened or solidified. Furthermore, especially a desirable constituent contains the material which can receive the thermal activation crosslinking reaction of a resin binder and said resin binder. As for this resin binder and a heat bridged compound, it is desirable that it is possible to dissolve into the solvent of non-reactivity or solvent mixture in the condition of not hardening, and it is possible to form a homogeneous non-adhesive adhesion thin film on the substrate front face where said binder and said heat bridged compound are applied on that front face.

[0015] Especially a desirable antihalation constituent contains the heat cross linking agent which uses an amine as a principal component, and the resin binder which uses a phenol as a principal component. The suitable heat cross linking agent which uses an amine as a principal component contains melamine-formaldehyde resin, glycoluril-formaldehyde resins, and the resin that uses a urea as a principal component. It is manufactured by American Cyanamid Company, Wayne, and New Jersey, and suitable melamine resin is a trade name. CymelR300, 301, 303, 350, 370, 380, 1116, and the melamine resin sold by 1130 are included. It is American Cyanamid Company at suitable glycoluril resin and the trade name of CymelR 1170, 1171, and 1172. The glycoluril resin sold is included. The suitable resin which uses a urea as a principal component is American Cyanamid Company at the trade name of BeetleR 60, 65, and 80. Such resin sold is included. It is American Cyanamid Company at the especially desirable cross linking agent which uses an amine as a principal component, CymelR 1123, and the trade name of 1125.

It is the material containing the benzoguanamine resin sold which uses benzoguanamine as a principal component. In addition, the combination including the combination containing the material which uses benzoguanamine as a principal component of the above-mentioned cross linking agent which uses an amine as a principal component will be suitable. American Cyanamid Company from -- the available above-mentioned resin -- in addition, the resin of much resemblances is commercially available from other feeders. in addition, such resin that uses an amine as a principal component -- the reaction of the acrylamide copolymer in the inside of a \*\* alcoholic solution or a methacrylamide copolymer, and formaldehyde -- or -- instead, it is possible to be prepared by copolymerization of N-alkoxy methylacrylamide or methacrylamide, and other suitable monomers. Generally the cross linking agent component of the antihalation constituent of this invention is used in about 5 - 50% of the weight of the amount of the solid-state sum total weight of the constituent, and is used still more typically in about 30% of the weight of the amount of the solid-state sum total weight of the constituent.

[0016] As mentioned above, as for the cross linking agent compound which uses the amine of this antihalation constituent as a principal component, it is desirable to be used combining the resin binder which uses a phenol as a principal component. The suitable resin binder which uses a phenol as a principal component, For example, novolak resin; Pori (vinyl phenol), Styrene Or alpha methyl styrene and Pori Copolymer [ with a (vinyl phenol) ]; acrylic resin; -- poly glutar imide; -- polyacrylic acid or polymethacrylic acid copolymer; -- alkali fusibility polyacrylamide copolymer and poly methacrylamide copolymer; -- 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate A polyvinyl alcohol; alkali fusibility styrene-allyl alcohol copolymer like the polyvinyl alcohol prepared from the polyvinyl acetate hydroxylated by the containing copolymer; partial target; such mixture is included.

[0017] A thing desirable in the above is novolak resin which has hydroxyl with Pori (vinyl phenol) and its copolymer, and has a part for the electrophilic substitution of an aromatic series ring in an alt.location or a para position to the hydroxyl. Combining with the resin which uses an amine as a principal component in an acid hardening resin system, usable novolak resin is about 300 - abbreviation 100,000. It is alkali fusibility thin film formation phenol resin within the limits of Dalton which has the molecular weight (weighted mean) of about 1000 to 20,000 Dalton within the limits preferably. These novolak resin can be prepared by the condensation reaction of a phenol, a naphthol, a substitute phenol (for example, cresol, a xylenol, ethylphenol, butylphenol, an oxy-propyl methoxy phenol, chlorophenol, a BUROMO phenol, resorcinol, a naphthol, a chloro naphthol, a BUROMO naphthol, a hydroquinone), and a formaldehyde, an acetaldehyde, a benzaldehyde, a furfural, an acrolein or its prototype. In order to adjust the dissolution rate of an exposure coat in a basic aqueous solution, the blend of suitable novolak resin can still also be used in order to adjust the physical characteristic of the viscosity of the coat, hardness, and others. Suitable novolak resin is indicated by much patents containing U.S. Pat. No. 3,148,983, 4,404,357, 4,115,128, 4,377,631, 4,423,138, and 4,424,315, and the content of disclosure of these patents is included in this book as a reference matter.

[0018] Pori (vinyl phenol) is thermoplastics which can be formed of the block polymerization or emulsion polymerization of the monomer which corresponds while a cation catalyst exists, or solution polymerization. the vinyl phenol used for generation of Pori (vinyl phenol) resin -- for example, it is possible to be commercially prepared by hydrolysis of an available coumarin or an available substitute coumarin and the decarboxylation of the hydroxy cinnamic acid obtained as the result following it. an usable vinyl phenol -- dehydration of the corresponding hydroxyalkyl phenol -- or it is also possible to be prepared by the decarboxylation of the hydroxy cinnamic acid obtained as a result of substitute or the reaction of an unsubstituted hydroxy benzaldehyde and a malonic acid. The desirable Pori (vinyl phenol) resin prepared from such a vinyl phenol is about 2,000 - abbreviation 100,000. It has the molecular weight range of Dalton. The generation method of Pori (vinyl phenol) resin can be found out by U.S. Pat. No. 4,439,516 included in this book as a reference matter.

[0019] Another suitable resin binder which uses the phenol for using it in the antihalation constituent of this invention as a principal component is the copolymer of a phenol unit and a cyclic alcohol unit structurally similar to novolak resin and Pori (vinyl phenol) resin. Such a copolymer is explained to the United States Patent application application numbers 07/354,800 included in this book as a reference

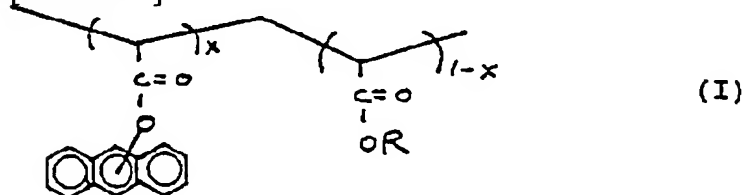


matter. These copolymers can be generated by some methods. For example, in the conventional preparation of Pori (vinyl phenol) resin, cyclic alcohol is added to that reaction mixture as a comonomer during a polymerization reaction, and, after that, this polymerization reaction is performed by the usual method. Although it is desirable that it is aliphatic series as for this cyclic alcohol, you may also include 1-2 double bonds. As for this cyclic alcohol, it is desirable that it is cyclic alcohol structurally nearest to a phenol unit. For example, the comonomer will be a vinyl cyclohexanol if the resin is Pori (vinyl phenol).

[0020] The desirable method for generation of this copolymer includes hydrogenation of the Pori (vinyl phenol) resin generated beforehand. Hydrogenation can be carried out by [ which pass a reduction catalyst top like the carbon base which used the well-known hydrogenation method by this work, for example, was covered with platinum or palladium in the solution of phenol resin ] depending especially or passing a Raney nickel catalyst top by the high voltage force and high temperature preferably. The concrete terms and conditions are decided by the polymer which should be hydrogenated. Furthermore, especially for this polymer, it dissolves into a suitable solvent like ethyl alcohol or an acetic acid, and is after that, and that solution is about 50-300. It is contacted to the Raney nickel catalyst which is the temperature of about 100 - 300 \*\*, and was pulverized under the pressure of an atmospheric pressure or an atmospheric pressure higher than it. This pulverized nickel catalyst may be any of a "carbon top nickel" catalyst also with a "silica top nickel" catalyst or an "alumina top nickel" catalyst according to the resin which should be hydrogenated.

[0021] Another suitable resin binder for the antihalation constituent of this invention is the polymer containing an anthracene unit. This polymer may contain other units like the carboxy and/or alkyl ester YUNINTO which hung from the polymer frame. Especially a desirable resin binder has the structure of a degree type (I), [0022]

[Formula 1]



In a before type, it is R. It is one hydrogen or one alkyl group (for example, alkyl group which has 1-6 carbon atoms), and is x. It is the mole fraction of the anthracene ester unit in that polymer, and is this x. 0.1-1.0 It is suitable that it is a value. Such an anthracene radical does not need to be replaced or may be replaced by substituent like a halo or alkoxy \*\* alkyl in one or more replaceable locations.

Appropriately, this anthracene portion can be replaced by one carboxyl group in the replaceable location of the arbitration of that anthracene ring, as the formula (I) was shown above. It is desirable that this resin binder contains 9-anthracene ester unit. Such an anthracene resin binder can be prepared by the condensation of a vinyl ester resultant with other polymerization possible compounds for generating anthranol and chlorination methacryloyl condensation, condensation of the vinyl anthracene ester resultant for generating the homopolymer following it, or mixed polymer.

[0023] In order to reinforce the etching-proof nature of an antihalation constituent, a silicon content material like Pori (vinyl silsesquioxane) is usable. Such silicon content resin can be used possible [ being independently used as a resin binder of an antihalation constituent ], being combined with other resin binders like the above-mentioned phenol resin.

[0024] The concentration of the resin binder component of the antihalation constituent of this invention can be changed within comparatively large limits, and generally, this resin binder is about 50 - 95% of the weight of the concentration of the sum total weight of the desiccation component of that constituent, and, more typically, is used by about 60 - 80% of the weight of the concentration of that desiccation component sum total weight.

[0025] As mentioned above, the antihalation constituent of this invention is the acid or acid generator

compound (acid generator compound) for carrying out the catalyst of the crosslinking reaction between said resin binders and said cross linking agent compounds further. You may contain. It is desirable that an acid generator compound is used. A suitable acid generator compound contains the compound which separates an acid by the photolysis or heat treatment. For example, it is desirable that a heat acid generator (thermal acid generator) like the compound which generates an acid by heat treatment is used. For example, well-known various heat acid generator compounds like 2, 4, 4, and 6-tetrabromo cyclohexa JIENON, benzoin tosylate, 2-nitrobenzyl tosylate, and the alkyl ester of an organic sulfonic acid are appropriately used in the acid-resisting constituent of this invention. Typically, the content of the heat acid generator in an antihalation constituent is about 1 - 15% of the weight of the sum total weight of the desiccation component of the constituent, and is about 5 of desiccation component sum total weight still more preferably. It is weight %. an onium salt and 1 and 1-screw [p-chlorophenyl] - a photo-oxide generating agent (photoacid generator) like a halogenation nonionic photo-oxide generating agent like 2, 2, and 2-trichloroethane, and other photo-oxide generating agents indicated in this book for using it in a photoresist constituent It may be used in an antihalation constituent. Generally the suitable amount of the photo-oxide generating agent in an antihalation constituent is about 1 - 15% of the weight of the sum total weight of the desiccation component of the constituent. In the case of the antihalation constituent containing a photo-oxide generating agent, the enveloping layer of the constituent is the photo-oxide (photoacid). It is put to activation radiation of an amount effective in making it generate, and it is after that and stoving of a postexposure is performed at sufficient temperature to stiffen the enveloping layer selectively at least.

[0026] the antihalation constituent of this invention does not use an acid catalyst -- or it should be understood by using the acid catalyst of non-light activity like a heat acid generator that it is possible for it to be non-light image formation nature (non-photoimageable). Or what the antihalation constituent is made into optical image formation nature for (therefore, development is made possible) is possible mixing a photo-oxide generating agent with a suitable effective dose into the constituent, and by exposing the enveloping layer of the constituent through a photo mask after that. A suitable photo-oxide generating agent contains the photo-oxide generating agent by which nonionic [ which is explained in this book ] was halogenated.

[0027] The additive of another arbitration of the constituent of this invention is a compound which absorbs the radiation used in order to expose a finishing photoresist layer and which works as a color. The specific photoresist used will mainly opt for selection of the color which should carry out extinction of this color good in the wavelength of the radiation which exposes a finishing photoresist, therefore was suitable for the specific antihalation constituent. For example, when using an acid-resisting constituent, combining it with a \*\* U.V. photoresist (namely, resist exposed among 100-300nm), in the \*\* U.V. field, extinction of the color compound should be carried out powerfully. A suitable color is well-known at this work, for example, it is [ a curcumine group, its derivative, an anthracene anthra ROBIN Sudan Orange, benzo phenothiazin, and ] Naphthol AS. It contains. Typically, the concentration of the color contained in an antihalation constituent is about 2 - 30% of the weight of the sum total weight of the desiccation component of the constituent, and is five to 15 amount [ of the sum total weight of the desiccation component of the constituent ] % more preferably.

[0028] the additive of other arbitration -- for example, Union Carbide from -- trade name Silwet 7604 \*\*\*\*\* -- a leveling agent like an available leveling agent (leveling agent) is included.

[0029] In order to make a liquid coat constituent, the component of said antihalation constituent For example, ester like one or more glycol ether; N-methyl pyrrolidinone; methyl-cellosolve acetate, ethylcellosolve acetate and propylene-glycol-monomethyl-ether acetate like 2-methoxy ethyl ether (diglyme), ethylene glycol monomethyl ether, or propylene glycol monomethyl ether, or dipropylene-glycol-monomethyl-ether acetate; it dissolves into a suitable solvent like other solvents like a dibasic acid ester, propylene carbonate, or gamma-butyrolactone. The concentration of the desiccation component in such a solvent will be determined by some elements like the method of application. Generally, the solid-state content of an antihalation constituent is about 1 - 50% of the weight of the sum total weight of the antihalation constituent, and is about 5 - 35% of the weight of the sum total weight of

the antihalation constituent preferably.

[0030] Various photoresists are able to be used with the antihalation constituent of this invention. When applied on the thin film layer of an antihalation constituent, it is desirable that the photoresist which can construct a bridge with the antihalation constituent in the interface of the two enveloping layers is used. Furthermore, especially the desirable photoresist for using it with the antihalation constituent of this invention contains the photo-oxide generating constituent containing the resin system which can construct a bridge with one or more components of an antihalation constituent of a positive type and a negative mold.

[0031] Especially the group of a desirable photoresist for using it with the antihalation constituent of this invention contains hardening, bridge formation, or the mixture of the material to solidify by contact in a photo-oxide generating agent compound, and heating and an acid. Desirable mixture is resin van IDA which uses a phenol as a principal component, and a cross linking agent which uses an amine as a principal component. The suitable resin which uses a phenol as a principal component contains novolak resin, and Pori (vinyl phenol) and its various copolymers. the cross linking agent of the above [ the suitable cross linking agent which uses an amine as a principal component ] for antihalation constituents -- especially -- American Cyanamid from -- available melamine-formaldehyde It is Cymel resin. A suitable photo-oxide generating agent compound contains a nonionic organic light activity compound like the halogenation light activity compound indicated by onium salt like the onium salt indicated by U.S. Pat. No. 4,442,197 by which each is included in this book as a reference matter, 4,603,101, and 4,624,912, and the Europe patent application referred to by the following. After these optical activity compounds are exposed by activation radiation, only sufficient amount to enable development of an enveloping layer must exist in a photoresist. The desirable negative-mold photoresist for the activity by this invention is the Europe \*\*\*\*\* by which the both are included in this book as a reference matter, for example. An acid solidification photoresist which is indicated by No. 0401499 and 0423446 is included. The nomenclature in the case of being used in this book "an acid solidification photoresist (acid-hardening photoresist)" means the photoresist constituent common type which is explained above and explained by said Europe patent application referred to.

[0032] Other desirable photoresists contain the positive type photoresist containing the component which can construct a bridge with one or more components of the antihalation constituent of this invention. Such a photoresist contains the resin binder which was combined with the radiation susceptibility component and which uses a phenol as a principal component. A suitable resin binder contains novolak resin, and Pori (vinyl phenol) and its various copolymers. A suitable radiation reception component is a 2, 1, and 4-diazo naphthoquinone sulfonate, a naphthoquinonediazide sulfonate like a 2, 1, and 5-diazo naphthoquinone sulfonate, an onium salt, and the Europe \*\*\*\*\* by which the both are included in this book as a reference matter. It is possible for various photo-oxide generating agent compounds containing other well-known acid generators like the acid generator currently indicated by No. 0164248 and 0232972 to be included. In addition to the "conventional" positive resist, the positive resist strengthened chemically is suitable for especially using it with the antihalation constituent of this invention. The positive resist strengthened chemically generates the optical product (photoproduct) of catalyst nature by exposure to activity radiation like the case of the above-mentioned acid solidification resist. The exposure field of that resist is made easier to dissolve in a developer by this optical product's (for example, acid's) carrying out the catalyst of the deprotection reaction of one or more resist components, and separating a polar functional group like carboxy by the positive type system. Solid State Technology besides Lamola "the resist (Chemically Amplified Resists) strengthened chemically" included in this book as a reference matter, and 53-60 (1991 year 8 moon) Please refer to.

[0033]

[Example] Now, drawing of an accompanying drawing showing the desirable operation of the antihalation constituent of this invention is referred to. Step A An antihalation constituent is applied to a substrate 10 in order to give the antihalation enveloping layer 12 then. The thing which include spin coating for this antihalation constituent and for which almost is applied with all standard means is

possible. Generally it is this acid-resisting constituent About 0.05-0.5  $\mu\text{m}$  It is about 0.10-0.20 micrometers preferably. It is desiccation layer thickness and applies on a substrate. This substrate may be which substrate appropriately used in former in processing containing a photoresist. For example, as for this substrate, it is possible for them to be the micro electronic wafer of silicon, the micro electronic wafer of a silicon dioxide, and the micro electronic wafer of an aluminum-aluminum oxide. It is also possible to use a gallium arsenide substrate, a ceramic substrate, a quartz substrate, and a copper substrate. For example, a glass substrate, an indium / tin coat substrate, and the substrate used for a liquid crystal display use like the prototype are also used appropriately.

[0034] Step B Halation \*\*\*\*\* is then stiffened selectively at least. The hardening condition will according to the component of an acid-resisting constituent. For example, probably, the temperature and the conditions of hardening will be higher than the temperature and the conditions containing an acid or an acid generator compound of hardening of a constituent, when the constituent does not include an acid catalyst. For example, a novolak resin binder and benzoguanamine-formaldehyde resins as a cross linking agent Cymel 1123 Hardening conditions typical in the case of the included constituent are heating of about 200 \*\* over for about 30 minutes. Heat acid generator 2, 4, 4, 6 - Probably, the curing temperature of about 150 \*\* over for about 30 minutes is suitable in order to stiffen that constituent enveloping layer selectively at least, when adding tetrabromo cyclohexa JIENON to this constituent. It is desirable that hardening conditions make an enveloping layer 12 insolubility substantially to a developer. In addition, as mentioned above, when an antihalation constituent contains a photo-oxide generating agent, it is possible making activation radiation (for example, about ten to 300  $\text{mJ}/\text{cm}^2$ ) of an effective dose expose the constituent enveloping layer, and by performing stoving of the postexposure of 50 - 140 \*\* after that to stiffen the constituent enveloping layer selectively at least.

[0035] Step C It applies on the front face of the antihalation layer 12 over which the bridge was then constructed in the photoresist. It is possible like the case of spreading of the antihalation constituent to apply a photoresist with a standard means like spin coating, dip coating, and roller coating. It is possible in spin coating, to adjust the solid-state content of a photoresist constituent so that desirable thin film thickness may be given based on the specific spin equipment used, the viscosity and the speed of spin equipment of the solution, and the amount of time amount usable to spin coating. In order to remove a solvent following spreading until a layer 14 becomes imprint resistance preferably, the photoresist enveloping layer 14 is typically dried with heating. Mutual mixing of an antihalation layer and a photoresist layer should not arise the optimal.

[0036] Step D Image formation is carried out to an enveloping layer 14 by activation radiation through a mask by the conventional method then. The exposure energy is magnitude sufficient since the pattern formation image 16 is produced in a layer 14 to activate the optical active ingredient of a radiation reception system effectively, it responds to the exposure instrument further especially typically, and the exposure energy is about ten to 300  $\text{mJ}/\text{cm}^2$ . It is a range.

[0037] Step E Since it is an optical step and the difference in the solubility between the exposure field of an enveloping layer and a non-exposing field is produced, when it is required for a photoresist to heat a postexposure, it is this step E. It is used. For example, typically, an acid solidification photoresist is a step. As postexposure heating is needed in order to trigger the crosslinking reaction by which the catalyst was carried out from the acid, as shown in E', and many of positives resist strengthened chemically are shown in step E'', postexposure heating is needed in order to trigger the deprotection reaction by which the catalyst was carried out from the acid. To the covered substrate 10, it is about 50 degrees C or more in temperature typically, and further especially, it is the temperature of about 50 to 140 \*\*, and stoving of a postexposure is performed.

[0038] Step F It is desirable to develop the resist enveloping layer 14 then exposed using an aqueous basicity developer like inorganic alkali (for example, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, a sodium hydrogencarbonate, a sodium silicate, a meta-sodium silicate, aqueous ammonia, or its prototype). hydroxylation fourth like the solution; tetraalkylammonium hydroxide which instead uses a choline as a principal component -- ammonium; ethylamine, n propylamine, diethylamine, or G n- various amine solution; like propylamine, triethylamine, or methyl diethylamine --

alcoholic amine; like diethanolamine or triethanolamine -- it is possible to use an organic developer called annular amines, such as a pyrrole and a piperidine. Generally, development follows a well-known method by this work.

[0039] In order to stiffen the developed exposure area 16 further following development in many cases, in the temperature of about 100 - 150 \*\*, final stoving of an acid solidification photoresist is performed for several minutes.

[0040] It is possible to process the developed substrate selectively after that on the substrate area where the photoresist was removed, for example, it is possible chemical etching or to galvanize by the well-known method by this work in the substrate area which removed the photoresist. A suitable etching agent includes a hydrofluoric-acid etching reagent and plasma gas etching like oxygen plasma etching. Especially plasma gas etching punches easily the antihalation enveloping layer over which the bridge was constructed.

[0041] In order to remove both many photoresists used for the antihalation constituent and this antihalation constituent of this invention, putting together, please care about that it is possible to use the same clearance chemical action. For example, the acid solidification photoresist used combining the desirable antihalation constituent containing said \*\*\*\*\* which uses as a principal component said resin binder to which a phenol is used as a principal component, and an amine of this invention can be easily removed after alternative substrate processing using one remover solution. In order to remove such an enveloping layer, a desirable remover solution contains about 90% of the weight of dimethyl sulfoxide, and about 10% of the weight of Para toluenesulfonic acid. It is desirable to use this constituent at about 70-90 degrees C.

[0042] In order to illustrate this invention more appropriately, the following examples are shown, but these examples are not constituted so that this invention may be limited only to the indicated specific example. In the antihalation constituent indicated in these examples, the novolak resin component is a formaldehyde-phenol condensate, and the phenol component is 95% of the weight of cresol, and 5. It is ethylphenol of weight % and the resin has the molecular weight (weighted mean) and about 20 degree of dispersion of about 11,000 Dalton.

[0043] an example 1 -- it prepared by mixing the component to which a desirable antihalation constituent is explained below. In addition, the amount of these components is expressed with the weight rate.

[0044]

Component Amount Resin binder Novolak resin 5.59 Cross linking agent material Hexamethoxy methyl melamine (product made from American Cyanamid) 1.67 Heat acid generator 2, 4, 4, 6-tetrabromo cyclohexa JIENON 0.28 Surface-water-of-aggregate common-ized agent Silwet 7604 (Union Carbide make) 0.015 Solvent Diglyme 33.96 Anisole 11.31 -- in order to make the thin film layer of this antihalation constituent into insolubility into an aqueous developer In order to determine required curing temperature, this antihalation constituent was examined. About the solution, it is 4000r.p.m on seven 4 inches silicon wafers by which the steamy first coat (for a HMDS steam, a room temperature, room pressure, and 3 minutes) was carried out. Spin coating was carried out. It is soft baking (soft baking) at temperature which is different to each for 60 seconds in each of these wafers on a vacuum hot plate. It carried out. Especially, stoving of each wafer was carried out for 20-degree C temperature increment in the temperature requirement of 80 - 200 \*\*. Thin film thickness was determined from seven measurement by Nanometrics Nanospec 215 which uses the refractive index of 1.64. Batch development of these seven wafers was carried out for 60 seconds in the MicropositR MF-321 developer (Shipley Co., Newton, aqueous hydroxylation TERATO methylammonium (TMAH) solution available from Massachusetts) of the room temperature of normality 0.21, and thin film thickness was again measured after that using Nanospec 215 as above-mentioned. 120 The stoving temperature more than \*\* is 0.21 N. It was discovered that it is sufficient temperature to construct a bridge in the HASHON stop enveloping layer so that a HASHON stop enveloping layer may be made into insolubility in a TMAH developer.

[0045] The antihalation constituent of example 2 example 1 was examined about the extinction in a \*\* U.V. field. On the 3 inches quartz wafer, the spin coating of the constituent was carried out by 3000

r.p.m, and it carried out soft baking by 120 \*\* for 60 seconds with the vacuum hot plate. The enveloping layer thickness was evaluated by measuring the enveloping layer thickness using Nanospec 215 as the 4 inches silicon wafer was covered with the bottom of the same conditions and it was explained by the above-mentioned example 1. Hewlett-Packard HP8452 A UV-Visible Spectrophotometer analyzed the coat wafer, and it amended about the absorbance of the quartz wafer after that. 248nm At exposure wavelength, the formulation is thickness 1. Per [ 1.371 ] micron It discovered having the absorbance of an absorbance unit.

[0046] The spin coating of the antihalation constituent of example 3 example 1 was carried out in 3000r.p.m. on four 4 inches silicon wafers by which the steamy first coat (procedure as explained to the HMDS steam and the example 1) was carried out. Soft baking of each of these wafers was carried out for 60 seconds on the vacuum hot plate. Stoving of the two wafers was carried out by 140 \*\*, and stoving of other two wafers was carried out by 160 \*\*. After that, it is each of these four wafers 3660 r.p.m. The spin for [ it can set ] 30 seconds is used, it finishes by the Megaposit SNR248-1.0 \*\* UV photoresist (acid solidification photoresist sold by Shipley Co.), it is followed, and it is about 1.025. Since the resist layer thickness of a micron was produced, soft baking was carried out for 60 seconds at 90 degrees C on the vacuum hot plate. About these wafers, it is 248nm. GCA Laserstep which works on wavelength It exposed using the excimer laser stepper. 8x8 which includes both wide range exposure and focal adjustment in order to make to obtain the optimal exposure into a positive thing The pattern of an array was used. These wafers were divided into two groups and the coat wafer of another side stiffened [ the group / by 140 \*\* / by while ] in each and stiffened by the coat wafer and 160 \*\* was included. To the group of one wafer, in 110 \*\*, postexposure stoving was performed for 60 seconds on the vacuum hot plate, and stoving of the group of another side was carried out by 140 \*\*. It paddling for 25 seconds and 50 seconds, and a total of 100 in all these wafers. The developer contact time of a second is used and it is TMAH MF-319 of 0.14 N in duplex paddling mode. Developer (Shipley Co.) Negatives were used and developed. On the antihalation enveloping layer, it is 0.34 micrometers. Pattern formation of the line/the gap of the high resolution of until (the line which has a in general vertical side attachment wall is included) was carried out.

[0047] an example 4 -- it prepared by mixing the component to which another desirable antihalation constituent is explained below. In addition, the amount of these components is expressed with the weight rate.

[0048]

Component (American Cyanamid) Amount Resin binder Novolak 3.462 Cross linking agent material It sells by the trade name Cymel 1123. Ethylation/methylation benzoguanamine-Holum Al as whom it acts DEHIDO resin 1.039 Solvent Diethylene-glycol wood ether 25.500 -- the spin coating of this antihalation constituent was carried out in 4600r.p.m. on the 4 inches silicon wafer by which the steamy first coat (for a HMDS steam, a room temperature, room pressure, and 3 minutes) was carried out, and the 4 inches quartz wafer by which a first coat is not carried out. In 125 \*\*, soft baking of each wafer was carried out for 60 seconds on the vacuum hot plate. After that, they are those wafers. Blue M Stoving was carried out for 30 minutes in the convection-current furnace. Thickness analysis of the antihalation constituent coat silicon wafer by NanometricsNanospec 215 showed the average thin film thickness of 1733A. Cary3 UV-Visible Spectrophotometer analyzed the quartz wafer. after the amendment about the absorbance of the quartz wafer -- the absorbance of an antihalation coat quartz wafer with a thickness [ the ] of 1733A -- 248nm wavelength -- setting -- 0.719 (absorbance unit) it is -- things were discovered. To the degree, it is one coat silicon wafer. It finished by 248 to MegapositR SNR1.0 photoresist, and another coat silicon wafer was finished by MicropositR XP-89131 photoresist. in addition, each of said photoresist -- both -- Shipley Co. from -- it is available. Megaposit SNR248 Coat of a resist, About 1.014 It is 3680 r.p.m. in order to produce the thickness of a micron. The 2nd 90-degree C soft baking for [ of an on / a vacuum hot plate ] the spin for [ it can set ] 30 seconds and 60 seconds is needed, and, on the other hand, it is Microposit. XP-89131 resist is 1.017. In order to obtain the enveloping layer of the thickness of a micron, it is the spin of 3760r.p.m. The \*\*\*\*\* drying temperature of 110 degrees C was needed. GCA Laserstep which commits these two wafers on the

wavelength of 248nm It exposed using the excimer laser stepper. In order to make to obtain the optimal exposure into a positive thing, the pattern of 7x15 arrays which include both wide range exposure and focal adjustment was used. To all these wafers, stoving of a postexposure is performed by 130 \*\* for 60 seconds on a vacuum hot plate, and it is paddling for 25 seconds and 50 seconds, and a total of 100 after that. The developer contact time of a second was used and negatives were developed in duplex paddling mode using the XP-89114 aquosity developer (TMAH developer available from Shipley Co.). On the antihalation enveloping layer, it is 0.36 micrometers. Pattern formation of the line/the gap of the high resolution of until (the line which has a in general vertical side attachment wall is included) was carried out.

[0049] It is understood that the deformation and alteration are able to be performed without deviating from the range or thought of this invention as the above-mentioned explanation of this invention only illustrates this invention and it is stated to this patent claim.

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[Translation done.]



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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is explanatory drawing showing the process of this invention roughly.

[Description of Notations]

10 Substrate

12 Antihalation Enveloping Layer

14 Photoresist Enveloping Layer

16 Pattern Formation Image

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[Translation done.]



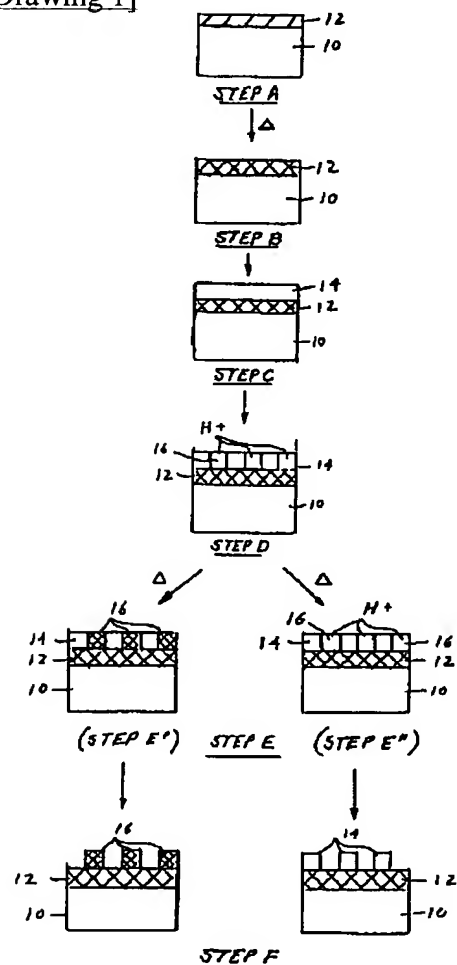
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## DRAWINGS

[Drawing 1]



[Translation done.]